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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US92/03483 <b>(22) International Filing Date:</b> 24 April 1992 (24.04.92) <b>(30) Priority data:</b> 692,008 26 April 1991 (26.04.91) US <b>(71) Applicant:</b> VISTA CHEMICAL COMPANY [US/US]; 12025 Vista Park Drive, Austin, TX 78726 (US). <b>(72) Inventors:</b> BEGGS, Ronald, L. ; 504 Country Glen Drive, Leander, TX 78641 (US). LEWIS, Duane, J. ; 411 Duck Lake Drive, Austin, TX 78734 (US). MADDERRA, Gal- an, K. ; Route 2, Box 272, Ponca City, OK 74601 (US). DECKER, Lewis, Bernard, Jr. ; 20625 Highland Lake Loop, Lago Vista, TX 78645 (US).		<b>(74) Agent:</b> BUSHMAN, C., James; Browning, Bushman, An- derson & Brookhart, 5718 Westheimer, Suite 1800, Houston, TX 77057 (US). <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (Eu- ropean patent), GN (OAPI patent), GR (European pa- tent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC (European patent), MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (Euro- pean patent), NO, PL, RO, RU, SD, SE, SE (European patent), SN (OAPI patent), TD (OAPI patent), TG (OA- PI patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR PREPARING SUB-MICRON ALUMINA PARTICLES		
<b>(57) Abstract</b>  A process for producing particulate anhydrous alumina of sub-micron particle size comprising calcining a hydrated alumi- na having a surface area of from about 3 to about 90 m <sup>2</sup> /g to produce anhydrous alumina which when de-agglomerated forms an anhydrous alumina powder having an average particle size less than about one (1) micron, the hydrated alumina conve- niently being obtained by treating a mixture of an aqueous medium and an anhydrous alumina precursor such as boehmite at a temperature of greater than about 250 °F, a pressure sufficient to prevent any substantial loss of water at the treating temperature and for a length of time to produce a slurry containing a hydrothermally treated alumina having the desired surface area which is then recovered from the slurry, dried and calcined.		

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**PROCESS FOR PREPARING SUB-MICRON ALUMINA PARTICLES****Background of the Invention****1. Field of the Invention**

The present invention relates to the preparation of anhydrous, e.g. alpha, alumina powders having high purity and uniform, small particle size, i.e., less than about one (1) micron. More particularly, the present invention relates to a process for producing sub-micron alpha alumina powder without the need for intensive mechanical grinding.

**2. Description of the Background**

In many applications, high purity, small, uniform particle size anhydrous, e.g. alpha, alumina powders are required. For example, in the production of high technology ceramics it is known that the use of small, uniform particle size alpha alumina results in end products which are less susceptible to fracturing or other mechanical failure. Currently known technology for producing small, uniform particle size alpha alumina powder consists in firing hydrated aluminas, e.g. alumina trihydrates or monohydrates, at high temperatures to convert the hydrated alumina to the desired alpha phase. During this conversion, as is well known in the art, the small crystals of the alpha alumina precursors sinter into larger particles made up of clusters of alpha alumina crystals. In order to achieve the desired sub-micron size, it is thus necessary to subject the strongly agglomerated alpha alumina particles to intensive mechanical grinding, e.g. ball milling. Not only is this expensive and time consuming, but it rarely leads to a uniform particle size of the end product alpha alumina powder. Moreover, the intensive grinding invariably introduces impurities (from the grinding equipment) into the end product alpha alumina powder which ultimately end up in the ceramic products produced from the powder. These impurities coupled with the non-uniform size of the alpha alumina particles set up mechanical weak points in the ceramic products produced subjecting them to stress and easy fracture.

Summary of the Invention

It is therefore an object of the present invention to provide an improved process for producing anhydrous alumina of uniform, small particle size.

It is another object of the present invention to provide a process for producing small  
5 particle size alpha alumina powder which eliminates the need for extensive mechanical grinding.

Another object of the present invention is to provide a process for providing small particle size alpha alumina powder which is substantially free from impurities normally introduced from intensive mechanical grinding.

10 Still a further object of the present invention is to provide a method for controlling the particle size of an anhydrous alumina powder by controlling the surface area/crystal size of an anhydrous alumina precursor used to produce the powder.

The above and other objects of the present invention will become apparent from the description given herein and the appended claims.

15 According to one aspect of the present invention, a hydrated alumina having a surface area of from about 3 to about 90, preferably from about 10 to about 70, m<sup>2</sup>/g is calcined under conditions which produce an agglomerated anhydrous alumina, the agglomerated anhydrous alumina being de-agglomerated to produce an anhydrous alumina powder having an average particle size of less than about one (1) micron.

20 According to another aspect of the present invention, a mixture of an aqueous medium and an anhydrous alumina precursor is treated at a temperature greater than about 250°F and at a pressure equal to or greater than about the vapor pressure of water at the treating temperature for a period of time sufficient to produce a slurry containing a hydrothermally treated alumina having a surface area of from about 3 to about 90, preferably from about 10

to about 70, m<sup>2</sup>/g. The hydrothermally treated alumina is recovered from the slurry, dried and calcined to produce an anhydrous alumina product which when de-agglomerated produces an anhydrous alumina powder having an average particle size of less than about one (1) micron.

Brief Description of the Drawing

The single figure is a graph showing the relationship of final, milled particle size alpha alumina to starting boehmite surface area (crystal size).

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Description of the Preferred Embodiments

The discovery of the present invention is that by calcining a hydrated alumina having a surface area of from about 3 to about 90, preferably from about 10 to about 70, m<sup>2</sup>/g to produce an anhydrous alumina agglomerate and de-agglomerating, e.g., grinding, the agglomerate, it is possible to obtain a high purity anhydrous alumina powder having an average particle size of less than about one (1) micron. Although the hydrated alumina having the required surface area can be obtained from natural sources, in practice it is conveniently obtained by the hydrothermal treatment of an anhydrous alumina precursor. The term anhydrous alumina precursor, as used herein, refers to any hydrated alumina which upon heating to a given temperature, depending upon the particular hydrated alumina, will convert to Al<sub>2</sub>O<sub>3</sub>, e.g. alpha alumina, gamma alumina, delta alumina, etc. For purposes of describing the invention with particularity, the term "alpha alumina" will be employed, it being understood that the description is equally applicable to any anhydrous alumina. Non-limiting examples of suitable anhydrous alumina precursors include pseudoboehmite, boehmite, bayerite, diaspore, etc., whether obtained from natural or synthetic sources. A preferred alpha alumina precursor comprises a pseudoboehmite or boehmite alumina. The preferred boehmite, alpha alumina precursor, may be either of the water-dispersible type such as disclosed in U.S. Patent No. 4,676,928 or of the acid-dispersible type such as disclosed in U.S. Patent No. 4,746,503. Boehmite is commonly obtained synthetically by the hydrolysis of aluminum alkoxides in the well known fashion. Typical methods for preparing such aluminum alkoxides are shown, for example, in U.S. Patent No. 4,242,271, incorporated herein by reference for all purposes. The aluminum alkoxide can be hydrolyzed, in the well known manner, such as by the process taught in U.S. Patent No. 4,202,870, incorporated herein by reference for all purposes. Especially preferred are

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boehmite aluminas obtained from the hydrolysis of aluminum alkoxides derived from Ziegler Chemistry in the well known manner. However, it will be recognized that boehmite alumina from other sources can be formed into slurries and used in the process of the present invention.

5           In conducting the process of the present invention to provide a source of hydrated alumina having the required surface area, a mixture of an aqueous medium, e.g. deionized water, and the alpha alumina precursor is formed, the alpha alumina precursor generally being present in an amount of from about 1 to about 35% by weight calculated as  $Al_2O_3$ . In forming the mixture of the alpha alumina precursor and the aqueous medium, other additives  
10       can be incorporated so long as they do not adversely affect the crystal growth of the alpha alumina precursor. For example, the addition of carbon dioxide, acids, etc. can be tolerated provided there is no interference with obtaining the desired surface area via crystal growth.

          The mixture (slurry) of the aqueous medium and the alpha alumina precursor, once formed, is subjected to an elevated temperature of greater than about 250°F, preferably from  
15       about 300°F to about 900°F, especially from about 350°F to about 750°F, for a period of time sufficient to produce a slurry containing a hydrothermally treated alumina having a surface area of from about 3 to about 90, preferably from about 10 to about 70,  $m^2/g$ . Generally the pH will be maintained in a range of from about 3 to about 11. It will be appreciated that the desired surface area/crystal size can be obtained either by using lower  
20       temperatures and longer treating times or higher temperatures and shorter treating times. In general, the desired surface area can be obtained in a time frame of from about 1 hour to about 5 days again depending upon the temperature employed, the starting material, etc. Although high pressures can be employed, e.g., about 5 to about 220 atmospheres or greater, it is generally only necessary to conduct the hydrothermal treatment at a pressure

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approximately at or above the vapor pressure of water at the particular treating temperature in order to prevent water loss by vaporization. The hydrothermal treatment can be carried out, preferably with agitation, although quiescent conditions may be employed.

5       Once the alpha alumina precursor has been hydrothermally treated sufficiently to obtain the desired surface area, which can be determined by methods well known in the art, the hydrothermally treated alumina is recovered from the slurry by spray drying, filtering, centrifugation or other well known methods. If necessary, e.g. if recovered by filtration, the recovered hydrothermally treated alumina is preferably dried, as for example by oven drying, and then fired or calcined to produce the alpha alumina end product.

10       In calcining the hydrated alumina having the desired surface area, the temperature employed will depend upon the nature of the alpha alumina precursor, i.e., whether prepared according to the hydrothermal process of this invention, obtained from naturally occurring sources, or prepared according to other methods. Thus, calcining temperature can range from about 900°C to about 1400°C, depending on the particular alpha alumina precursor  
15       employed. Generally speaking, however, calcining or firing temperatures of about 1000°C to about 1300°C are employed, particularly when the alpha alumina precursor is boehmite, the calcining being conducted for a period of time ranging from about 1 minute to about 4 hours. The calcining can be conducted in conventional calcining equipment well known in the art.

20       Calcining produces clusters of weakly agglomerated alpha alumina particles. To convert the agglomerate into the desired alpha alumina powder, it is only necessary to subject the agglomerated alpha alumina to a relatively mild mechanical grinding technique such as milling under conditions which do not result in a wearing away of the components of the grinding apparatus such that any significant amount of impurities from such components are

introduced into the alpha alumina powder. For example, whereas in prior art techniques intensive mechanical grinding, e.g. ball milling, is necessary to reduce the clusters of alpha alumina crystals to suitable sub-micron particle size, the agglomerations produced by the present invention are relatively loosely bound and the particles size of the alpha alumina making up the agglomerations are such that a relatively mild grinding technique such as jet milling (air impact) can be employed. In general, it can be stated that any de-agglomeration process which relies primarily on impingement of the agglomerates and/or particles thereof with one another to obtain the desired sub-micron size can be considered mild grinding, as that term is used herein, as distinguished from grinding which relies primarily on the agglomerates and/or particles thereof being reduced in size by virtue of being literally crushed between components of the grinding equipment.

It is desirable, for purposes of lowering calcining temperatures of the hydrothermally treated alpha alumina precursor, to introduce seed crystals of the alpha alumina, or other materials which are crystallographically similar, to the mixture of the aqueous medium and the alpha alumina precursor prior to the hydrothermal treatment, after the hydrothermal treatment prior to drying, or if desired, to the dry hydrothermally treated alpha alumina precursor. In the latter method, for example, the dried hydrothermally treated alumina precursor or a hydrated alumina from some other source can be dispersed in an aqueous medium and the alpha alumina seed particles added to the slurry, the slurry being agitated to produce a uniform mixture. The seed crystals of alpha alumina added will have an average particle size of less than one (1) micron and be added in an amount of from about 0.05 to about 90% by weight based on the weight of the alpha alumina precursor present. The addition of alpha alumina seed particles lowers the conversion temperature of the alpha alumina precursor to alpha alumina and aides in maintaining a looser agglomeration of the

alpha alumina obtained by calcining the hydrothermally treated alpha alumina precursor.

To more fully illustrate the present invention, the following non-limiting examples are presented.

Example 1

5 CATAPAL® or DISPAL® alumina, boehmite aluminas obtained from the hydrolysis of aluminum alkoxide produced by Ziegler Chemistry and marketed by Vista Chemical Company, were employed in all cases. In Runs 2-9 (See Table below) various mixtures of the aluminas (5 to 12% by weight  $\text{Al}_2\text{O}_3$ ) in aqueous mediums were prepared and hydrothermally treated at various temperatures ranging from about 350°F to about 650°F for  
10 varying periods of time ranging from about 8 hours to about 72 hours to obtain boehmite alumina having a range of surface areas (crystal size). The hydrothermal treatment was conducted at a pressure approximately at or slightly above the vapor pressure of water at the treating temperature to avoid loss of water during the hydrothermal treatment. CATAPAL® alumina was used as a comparison in Run 1.

15 Hydrothermally treated aluminas were recovered from slurries either by spray drying (Runs 2-5) or oven drying at 100°C at atmospheric pressure (Runs 6-9). The dried precursors were then calcined in a furnace at 1250°C for one hour. The calcined agglomerations of the alpha alumina were ground using a jet mill. In cases where the average crystal size of the starting boehmite was the proper size, the use of the jet mill was  
20 sufficient to completely de-agglomerate the alpha alumina, i.e. if the crystal size was too small or too large, sub-micron particle size was not obtained. As is well known, mild grinding techniques such as jet milling do not introduce impurities into the alpha alumina powder as a result of any significant wearing away of the contacting (grinding) components of the grinding apparatus. The surface areas of the de-agglomerated hydrothermally treated

alumina precursors were obtained by (BET) nitrogen adsorption.

The table below shows the relationship between the surface area of the hydrothermally treated alumina precursors and the average particle size of the alpha alumina obtained therefrom.

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RUN	ALPHA ALUMINA PRECURSOR		ALPHA ALUMINA
	SURFACE AREA (M <sup>2</sup> /G)	CRYSTAL SIZE 020 (Å)	AVERAGE PARTICLE SIZE (MICRONS)
1	260	35	2.0
2	110	110	2.6
3	49	390	0.57
4	40	480	0.32
5	34	560	0.29
6	16	> 600	0.62
7	5.5	> 2000	1.33
8	2.5	> 2000	1.89
9	1.5	> 2000	2.09

As can be seen, when the surface area of the hydrothermally treated alpha alumina precursor is maintained in a range of from about 3 to about 90 m<sup>2</sup>/g, more preferably from about 10 to about 70 m<sup>2</sup>/g, one can obtain an alpha alumina powder having an average particle size of less than about one (1) micron. The data in the Table is depicted graphically in the accompanying Figure. Moreover, because the powder can be obtained by jet milling, a relatively mild grinding technique, the powder is not contaminated with impurities from the grinding equipment, a common problem when intensive grinding (e.g. ball milling) is necessary to achieve a sub-micron size.

It has been found that if seeds of alpha alumina particles having an average particle

size of less than about one (1) micron are added, the hydrothermally treated alpha alumina precursor, particularly when boehmite is used, will convert to alpha alumina at a lower temperature. Moreover, the alpha alumina obtained on calcination is less agglomerated. Accordingly, this further enhances the ease of de-agglomerating the alpha alumina to the powder form. In using this seeding technique, the alpha alumina particles can be added to the mixture of the alpha alumina precursor and the aqueous medium prior to the hydrothermal treatment. Alternately, the dried, hydrothermally treated alpha alumina precursor can be dispersed in an aqueous system and the alpha alumina seeds added, the mixture then being agitated to produce a uniform dispersion. When this seeding technique is used, the alpha alumina seed particles are added in an amount of from about 0.05 to about 90% by weight of the alpha alumina precursor, an amount of from about 1 to about 25% by weight being particularly preferred. Actual experiments in using this seeding technique coupled with the hydrothermal crystal growing technique have shown that the calcining temperature can be lowered to about 1100°C which allows the use of conventional rotary calcining equipment equipped with metal alloy furnace tubes thus avoiding the need for expensive, fragile ceramic tubes. Boehmite alumina hydrothermally treated according to the process of the present invention must normally be calcined at a temperature of around 1250°C to obtain conversion to the alpha form. Additionally, because of the lower temperature, energy savings are achieved. Another advantage lies in the fact that alpha alumina powder produced at 1100°C is less strongly agglomerated than alpha alumina produced at higher temperatures.

As noted, while the hydrated alumina to be calcined and having the desired surface area can be obtained from any source, e.g. naturally occurring, it is conveniently prepared by the hydrothermal process of the present invention.

The foregoing disclosure and description of the invention is illustrative and explanatory thereof, and various changes in the method steps may be made within the scope of the appended claims without departing from the spirit of the invention.



What Is Claimed Is:

1. A process for producing sub-micron anhydrous alumina powder comprising:  
treating a mixture of an aqueous medium and an anhydrous alumina precursor at a  
temperature of greater than about 250°F and a pressure sufficient to prevent any substantial  
loss of water at the treating temperature for a period of time sufficient to produce a slurry  
5 containing a hydrothermally treated alumina having a surface area of from about 3 to about  
90 m<sup>2</sup>/g;  
recovering hydrothermally treated alumina from said slurry;  
calcining the hydrothermally treated alumina at a temperature and for a time sufficient  
to produce an anhydrous alumina product; and  
10 de-agglomerating the anhydrous alumina product to obtain an anhydrous alumina  
powder having an average particle size of less than about (1) micron.
2. The process of Claim 1 wherein the alumina product is alpha alumina.
3. The process of Claim 2 wherein said hydrothermal treatment is carried out at  
a temperature of from about 350°F to about 750°F for a period of time ranging from about  
1 hour to about 5 days.
4. The process of Claim 2 wherein said mixture contains from about 5 to about  
35 percent by weight alpha alumina precursor as Al<sub>2</sub>O<sub>3</sub>.
5. The process of Claim 2 wherein said alpha alumina precursor comprises  
boehmite.

6. The process of Claim 5 wherein said temperature is in the range of from about 350°F to about 750°F and the time is from about 1 to about 24 hours.

7. The process of Claim 2 wherein seed particles are introduced into said mixture prior to said hydrothermal treatment, said seed particles having an average particle size less than about one (1) micron.

8. The process of Claim 7 wherein said seed particles are added in an amount of from about 0.05 to about 90% by weight based on the weight of said alpha alumina precursor.

9. The process of Claim 2 wherein said seed particles are added to said hydrothermally treated alumina.

10. The process of Claim 9 wherein said seed particles are added in an amount of from about 0.05 to about 90% by weight based on the weight of said alpha alumina precursor.

11. The process of Claim 2 wherein said calcining is conducted at a temperature of from about 900°C to about 1400°C depending on the alpha alumina precursor used.

12. The process of Claim 11 wherein said calcining is conducted for a period of from about 1 minute to about 4 hours.

13. The process of Claim 2 wherein the surface area is from about 10 to about 70 m<sup>2</sup>/g.
14. The product produced by the process of Claim 1.
15. The product produced by the process of Claim 2.

16. A process for producing particulate anhydrous alumina of sub-micron particle size comprising:

calcining a hydrated alumina having a surface area of from about 3 to about 90 m<sup>2</sup>/g to produce an agglomerated anhydrous alumina; and

5 de-agglomerating the agglomerated anhydrous alumina to produce an anhydrous alumina powder having an average particle size of less than about one (1) micron.

17. The process of Claim 16 wherein the surface area is from about 10 to about 70 m<sup>2</sup>/g.

18. The process of Claim 16 wherein said hydrated alumina comprises boehmite.

19. The process of Claim 16 wherein said calcining is conducted at a temperature of from about 900°C to about 1400°C depending upon the hydrated alumina used.

20. The process of Claim 19 wherein said calcining is conducted for a period of from about 1 minute to about 4 hours.

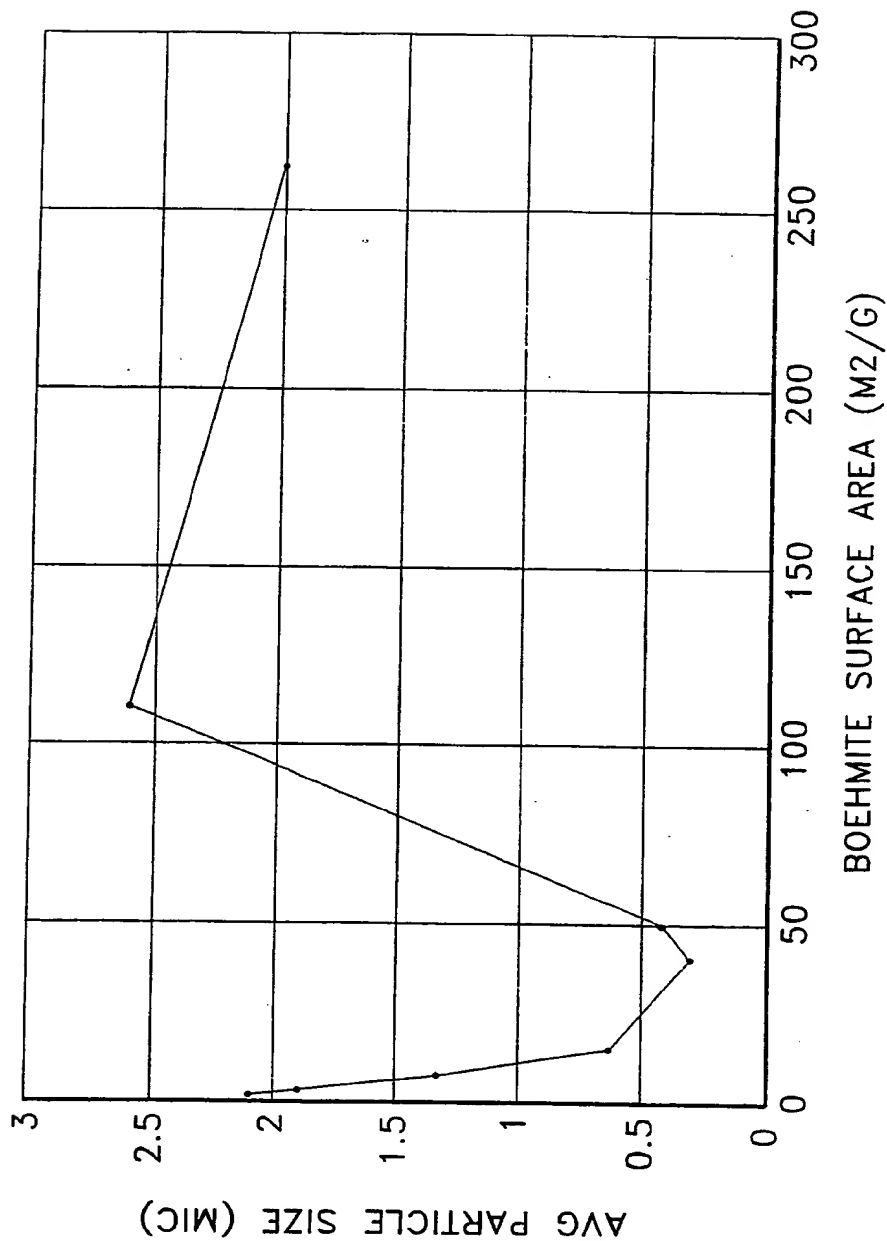
21. The process of Claim 16 wherein the anhydrous alumina is alpha alumina.

22. The anhydrous alumina powder produced by the process of Claim 16.

23. The alpha alumina powder produced by the process of Claim 21.

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# EFFECT OF BOEHMITE SURFACE AREA ON PRODUCT PARTICLE SIZE



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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/03483

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C01F 7/02

US CL : 423/625

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/626, 628, 629

501/153

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Automated Patent System - Hydrothermal? or Autoclav?  
Boehmite# or Alpha Alumina Monohydrates

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,797,139 (BAUER) 10 January 1989, See abstract; column 7, lines 5-7; Example III; claims 1-2,15.	1-15
Y	US, A, H189 (BAUER) 06 January 1987, See abstract; column 1, lines 7-13, 51-54.	1-15
Y	JP, A, 61-132,513 (ASAHI CHEM) 20 June 1986, See abstract.	1-15
Y	US, A, 4,117,105 (HERTZENBERG ET AL) 26 September 1978, See example 2.	16-23
Y	EP, A, 0,278,469 (BROWN) 17 August 1988, See abstract.	16-23
Y	The American Ceramic Society, 1970, Gitzen, "Alumina as a Ceramic Material," pp. 12-19, See figure 5.	16-23

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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